THE FISCHER-TROPSCH PROCESS: GASOLINE FROM COAL

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INTRODUCTION

The Federal Bureau of Mines was engaged from 1944 to about 1969 in a research and development program on the synthesis of gasoline and other Fischer Tropsch products from coal. The actual Fischer Tropsch reactor designs and catalyst work was done at Bruceton in what is now the Pittsburgh Energy Research Center of the U. S. Energy Research and Development Administration.

Historically the work was covered extensively by Storch.(1) This paper will cover the work done at Bruceton in the 1944-1969 period and the development of the various reactors and catalysts plus the present work.

OIL CIRCULATION PROCESS

The oil-circulation process was developed at Bruceton for synthesizing liquid fuels by the Fischer-Tropsch reaction.(2)(3) Carbon monoxide and hydrogen react over an iron catalyst to produce a product that is essentially hydrocarbons ranging from methane to high molecular weight wax. Removal of the heat of reaction (50,000 Btu/gallon of liquid product) is achieved by sensible heating of a recycle oil that completely covers the catalyst.

Although granular fused iron oxide (synthetic ammonia catalysts) used as a fixed-bed was active as a catalyst, gradual cementation of the particles together caused increased pressure drop. This problem was alleviated by operating with an expanded bed.(4) Because attrition caused gradual disintegration of the catalyst, catalysts with an inert core of iron and an external coating of catalytically active iron were developed such as oxidized ironshot. These experiments finally led to the development of lathe-turnings catalyst. This catalyst was used in a fixed-bed and showed no attrition problem, and the large void volume eliminated the problem of cementation. Table 1 shows data taken from this type of operation.

HOT GAS RECYCLE

The oil circulation system was limited in temperature and the hourly space velocity (SVH). The temperature could not be raised above 300° C without cracking and volatilizing the oil. The SVH could not be raised much above 800 without lowering the gas conversion. To overcome these problems, we turned to the hot-gas-recycle process.(5) This process uses a fixed bed of catalyst (lathe-turnings), through which large volumes of recycle gas are circulated to remove the heat of reaction as sensible heat. The lathe-turnings incurred a low pressure drop (about one psi/ft of bed height). Table 2 shows the results of several tests and shows the effects of some process variables on product distribution.

The parallel plate type catalyst was developed as a variant of the lathe-turning catalyst used in the hot-gas-recycle work. The pressure drop across this catalyst was significantly lower than that of the lathe-turning catalyst.(6)

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TABLE 1. - Typical experimental conditions and hydrocarbon yields in experiment 37 using steel lathe-turning catalyst in the oil-circulation process

Test period:	14	15	16
Catalyst age.....hr	1,503-1,527	1,551-1,671	1,671-1,791
Hourly space velocity of fresh gas.....hr^{-1}	700	601	600
Space weight velocity, ft^3(STP)/hr-lb Fe.....	8.74	7.51	7.51
Maximum pressure.....psig	310	312	313
Pressure differential.....psi	10	10	10
Maximum temperature.....° C	290	290	290
Temperature differential.....° C	7	6	6
Recycle-to-fresh gas ratio.....	2:1	2:1	2:1
CO_2 scrubbing.....	Yes	Yes	Yes
Synthesis gas ratio.....H_2:CO	1.018	1.014	1.025
Usage ratio.....H_2:CO	0.849	0.869	0.855
CO_2-free contraction.....volume-percent	65.1	63.6	57.8
H_2 conversion.....do.....	63.7	63.1	56.8
H_2+CO conversion.....do.....	70.0	68.3	62.3
CO conversion.....do.....	76.4	73.6	68.0
Ft^3 H_2+CO converted/lb Fe.....	6.12	5.13	4.68
Yields, g/m^3 H_2+CO converted:			
C_1.....	15.4	20.3	21.4
$C_2^=$.....	3.9	4.0	4.3
C_2.....	18.2	16.1	14.2
$C_3^=$.....	7.4	9.4	10.2
C_3.....	7.8	8.9	6.6
$C_4^=$.....	13.7	14.9	14.4
C_4.....	3.4	6.4	9.5
$C_5^=$.....	13.2	12.8	10.7
C_5.....	3.4	2.4	3.7
$C_6^=$.....	6.0	4.3	3.8
C_6.....	(1)	(1)	(1)
Light oil.....	68.9	61.9	62.4
Heavy oil.....	2.5	12.9	7.9
Aqueous layer.....	67.9	69.2	68.5
Product recoveries, lb/day:			
<204° C.....	18.24	15.88	14.71
204-316° C.....	4.11	3.00	2.89
316-450° C.....	1.92	1.71	1.63
>450° C.....	0.97	1.14	1.09
Product distribution, weight-percent:			
<204° C.....	72.3	73.0	72.4
204-316° C.....	16.3	13.8	14.2
316-450° C.....	7.6	7.9	8.0
>450° C.....	3.8	5.3	5.4
Relative catalyst activity[2].....	87	72	61
Recovery.....weight-percent	100.2	101.2	101.3

[1]None detected.

[2]Anderson, R. B., and others, Ind. and Eng. Chem., v. 44, 1952, pp. 391-397.

TABLE 2. - Effect of variables on product distribution[1]

Experiment and period	Reactor temperature change		Fresh gas H_2:CO ratio		Hourly space velocity		Percent water in recycle gas		Percent CO_2 in recycle gas		Chlorine deposition on catalyst		Potassium impregnation	
	11-A	11-B	16-D	16-F	8-H	8-K	7-D	7-C	7-J	7-K	13-A	13-B	8-C	9-C
Recycle to fresh feed ratio:														
Total	162	81	17	16	60	60	67	65	60	60	44	35	105	108
Cold	2.6	2.8	2.6	4.5	2.8	2.9	67	2.5	2.5	0	2.2	2.2	3.0	2.4
Average reactor temperature, ° C.	353	390	305	313	300	329	305	310	319	319	319	319	303	315
CO_2 in recycle gas, pct.	4.8	5.0	5.0	2.4	10.1	10.1	6.4	4.9	5.3	29.8	5.3	1.6	4.6	5.3
Water in recycle gas, pct.	-	-	4.3	4.9	4.1	4.0	0.2	2.5	5.0	7.3	5.1	7.3	3.4	4.8
Space velocity, vol./vol.-hr.	265	244	1,001	1,000	1,003	1,400	400	400	600	600	799	800	400	399
H_2:CO ratio:														
Fresh gas	1.41	1.23	1.36	2.91	1.29	1.30	1.28	1.31	1.29	1.29	1.40	1.46	1.28	1.33
Usage	0.96	1.02	1.26	2.61	1.16	1.15	1.21	0.97	1.09	0.73	1.13	1.73	1.16	1.18
Recycle	4.32	3.58	10.0	22.4	6.51	4.03	1.50	3.21	8.04	7.68	8.31	0.88	4.33	3.87
Weight-percent of hydrocarbons:														
C_1+C_2	30.1	48.3	47.3	59.5	33.9	32.1	17.3	25.7	19.5	24.9	25.6	18.8	38.0	21.4
C_3	4.2	6.8	16.5	17.5	13.0	11.2	0.5	1.3	3.1	3.7	3.3	2.5	15.2	3.1
Gasoline (C_3= - 204° C)	46.4	42.1	35.5	23.0	45.8	50.6	48.9	49.5	58.1	59.8	57.7	66.2	39.4	60.3
Diesel oil (204°-316° C)	7.1	2.5	0.7	0	6.8	5.8	13.0	10.2	11.3	6.7	6.7	7.7	3.6	10.4
Fuel oil + wax (316° C +)	12.2	0.3	0	0	0.4	0.3	20.3	13.3	7.4	4.9	6.7	4.8	3.8	4.8
Specific yield, g/m^3 H_2+CO converted:														
Oxygenates	8.8	7.5	2.5	3.8	5.9	5.4	10.8	8.1	9.6	6.2	9.0	2.6	3.3	8.9
C_2-C_6 olefins	41.3	37.5	10.7	7.5	18.1	31.6	28.5	34.6	39.0	74.4	41.3	51.5	16.9	44.3
Potassium oxide content on catalyst, wt-pct	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.16
Chlorine content on catalyst, wt-pct	-	-	-	-	-	-	-	-	-	-	[2]0.002	[3]0.05	-	-

[1]Underlined figures indicate change in variable.
[2]Chlorine content of oxidized and impregnated turnings similar to that used in experiment 13.
[3]Chlorine content of the discharged catalyst.

In this system catalysts are flame sprayed onto plates which then are assembled into parallel plate modules (figure 1) and stacked in the reactor. Originally a coating of synthetic ammonia catalyst (SAC) was used, but the most recent work used Alan Wood magnetite (AWM) impregnated with K_2CO_3. (7) Table 3 shows data from this work (Ex. 34) plus an experiment using the SAC (Ex. 33). Note the 2000 SVH achieved in the latest experiment and the greater proportion of gasoline-range hydrocarbons. This SVH is an economical feed rate considering the number of reactors necessary for a commercial plant.

SLURRY EXPERIMENTS

At the same time that the oil circulation system was being developed considerable work was proceeding on oil slurry operations. (8) In the slurry process, a finely divided fused iron catalyst (less than 5 microns) is kept in suspension in an oil (parafin oil--b.p. less than 384° C) by the agitation of synthesis gas rising through the slurry. In some of the experiments a new type catalyst, a nitrided iron catalyst, was used to attempt to maximize the yield of oxygenates, especially alcohols. Table 4 shows such data comparing the results of a test of the nitrided with the fused iron catalyst.

FLUIDIZED-BED TESTS

A series of tests were performed in a fluidized-bed also using a nitrided, fused iron catalyst. (9) The reactor was a 1-inch ss pipe, 6 feet long, enclosed in a 3-inch heat exchanger jacket. About 78 percent of the $1H_2$:1CO fresh feed was converted when the unit was operated at a SVH of 750, a 8:1 recycle-to-fresh feed gas ratio, a 300 psig pressure and a temperature of 252° C. About 33 percent of the total hydrocarbons made were oxygenates.

PRESENT WORK

Our present work in F.T. synthesis is based on the hypothesis that, because of the great change in the energy picture in the U. S., variations of the Fischer-Tropsch reaction may be economically viable. Cost studies (10) indicate that a modified SYNTHANE (11) coal-to-gas system where a Fischer-Tropsch reactor is substituted for the the methanation reactor and the H_2/CO ratio of the raw SYNTHANE gas is utilized, will yield a combination of substitute natural gas and light oil at minimum cost.

While the aim of the program at PERC is to use the Hot-Gas-Recycle pilot plant (with catalyst sprayed on parallel plates), the first experiment is being done in a bench-scale tube-wall reactor system. Figure 2 shows this reactor system and figure 3 a photo of an actual sprayed section.

The tube was a 3/4-inch stainless steel tube flame sprayed with a 0.020-inch coating of AWM; the coating was six inches in length. The magnetite was reduced with H_2 at 400° C. Then synthesis gas ($3H_2$ + 1CO) was introduced. Conditions of operation were: 1000 psig pressure and 310-315° C; flow rate was 4.37 scfh, equivalent to 1640 SVH (based on the annulus volume), or 30 scfh per sq. ft. of catalyst area, a more meaningful term for this type of operation. The heat of reaction was removed from the catalyst surface by boiling Dowtherm on the inside of the tube. Results of the first test are shown in table 5 where we operated at 300, 650 and 1000 psig.

Table 5 shows an increase in the C_1-C_4 alcohols with increasing pressure. The yield of hydrocarbons was low, as expected, because of the increased throughput (as given as scfh feed gas/ft^2 catalyst area). This also favored the formation of lighter hydrocarbons as shown in the wt-pct of the various hydrocarbon streams.

Planned tests include tests with Raney Iron before changing the H_2/CO ratio in the feed gas.

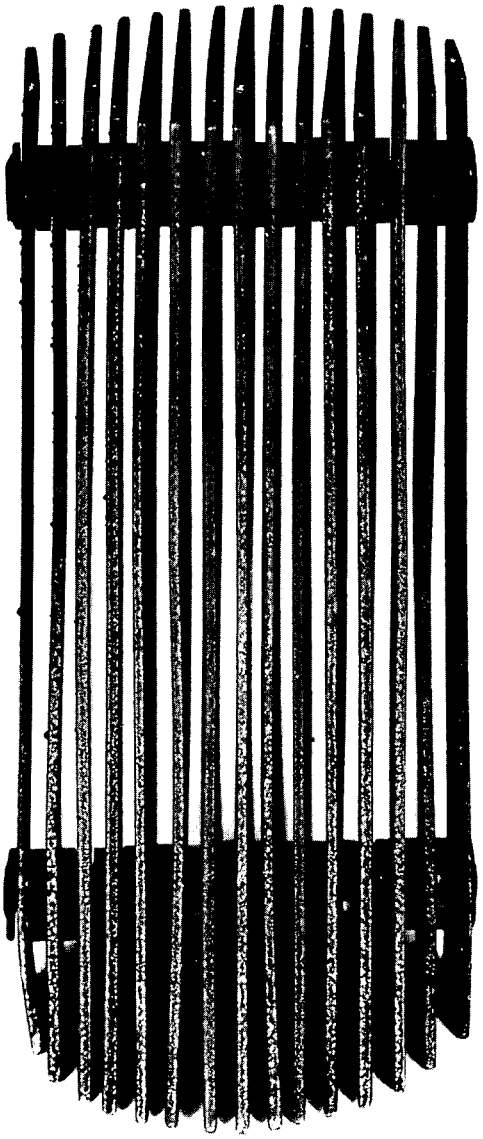
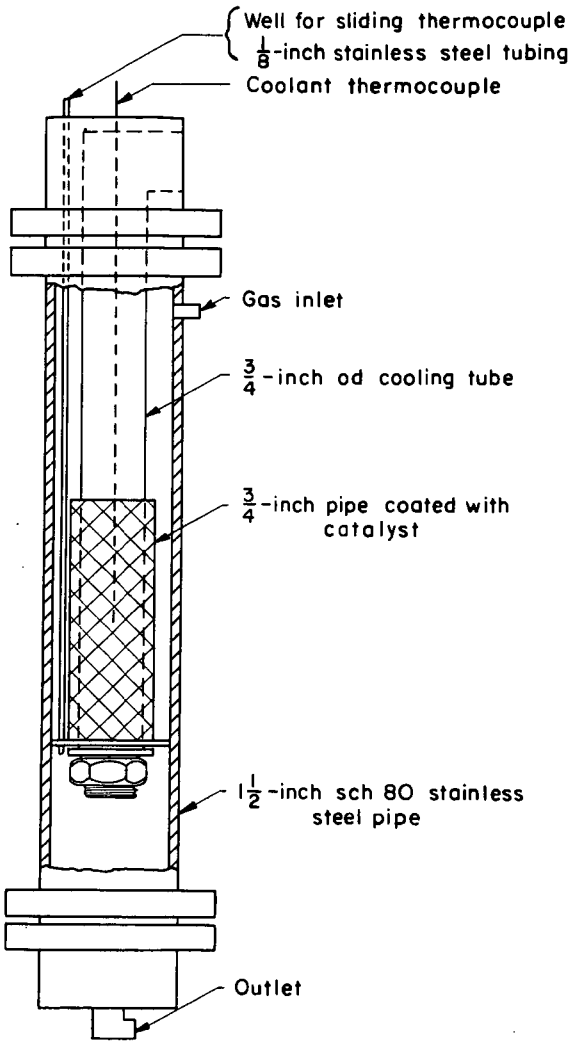


TABLE 3. - Hot-gas recycle synthesis results with flame-sprayed catalyst-coated plate assemblies

	Exp. No. HGR 33		Exp. No. HGR 34	
Fresh gas space velocity, vol/vol hr	600	1000	1000	2000
Total recycle in fresh feed, vol/vol	52	15.9	20.4	14.4
Reactor pressure, psig	400	400	400	400
Catalyst temperature, °C				
Average	269	325	320	325
Differential	20	50	40	50
H_2 conversion, pct	73.4	90.9	90.1	83
CO conversion, pct	80.6	98.8	98.2	94.4
H_2+CO conversion, pct	76.4	94.4	93.4	87.5
Overall weight balance, pct	93.6	90.8	87.8	96.6
Hydrocarbons recovered, lb/1000 SCF fresh gas	7.4	9.5	10.3	11.6
Hydrocarbons recovered, wt-pct				
C_1+C_2	59.7	36.5	33.9	29.5
C_3	6.6	14.1	13.3	12.8
Gasoline ($C_3^=$ <240° C	31.8	43.7	48.5	53.0
Diesel oil (204°-316°C)	1.9	5.0	4.0	3.8
Fuel oil (316°-450° C)	0	0.4	0.2	0.5
Wax (>450° C)	0	0.3	0.1	0.4

TABLE 4. - Slurry Test Data

Experiment No	LP-99	LP-66
Catalyst	Fused Iron	Nitrided Fused Iron
Space Velocity, scfh/ft^3 volume	300	300
Temperature	255° C	250° C
H_2+CO Conversion, pct	69.7	46.6
Usage Ratio	1.02	0.84
Yield gm/m^3 (H_2+CO) Converted:		
C_1-C_2	20.0	44.4
Gas C_3-C_6	39.2	67.4
Light Oil	78.8	55.4
Heavy Oil	47.3	0.0
Aqueous Layer	90.5	65.0
Yield C_3^+	165.3	154.1
Oxygenates	6.9	44.9
Infrared Analysis of Light Oil, wt-pct:		
OH	2.1	10.9
COOH, COO, CO	1.2	1.8
C=C	10.21	5.3
Aqueous Product:		
Oxygenated Compounds:		
(KFR) wt-pct	4.3	58.2


Well for sliding thermocouple
1/8-inch stainless steel tubing
Coolant thermocouple
Gas inlet
3/4-inch od cooling tube
3/4-inch pipe coated with catalyst
1 1/2-inch sch 80 stainless steel pipe
Outlet

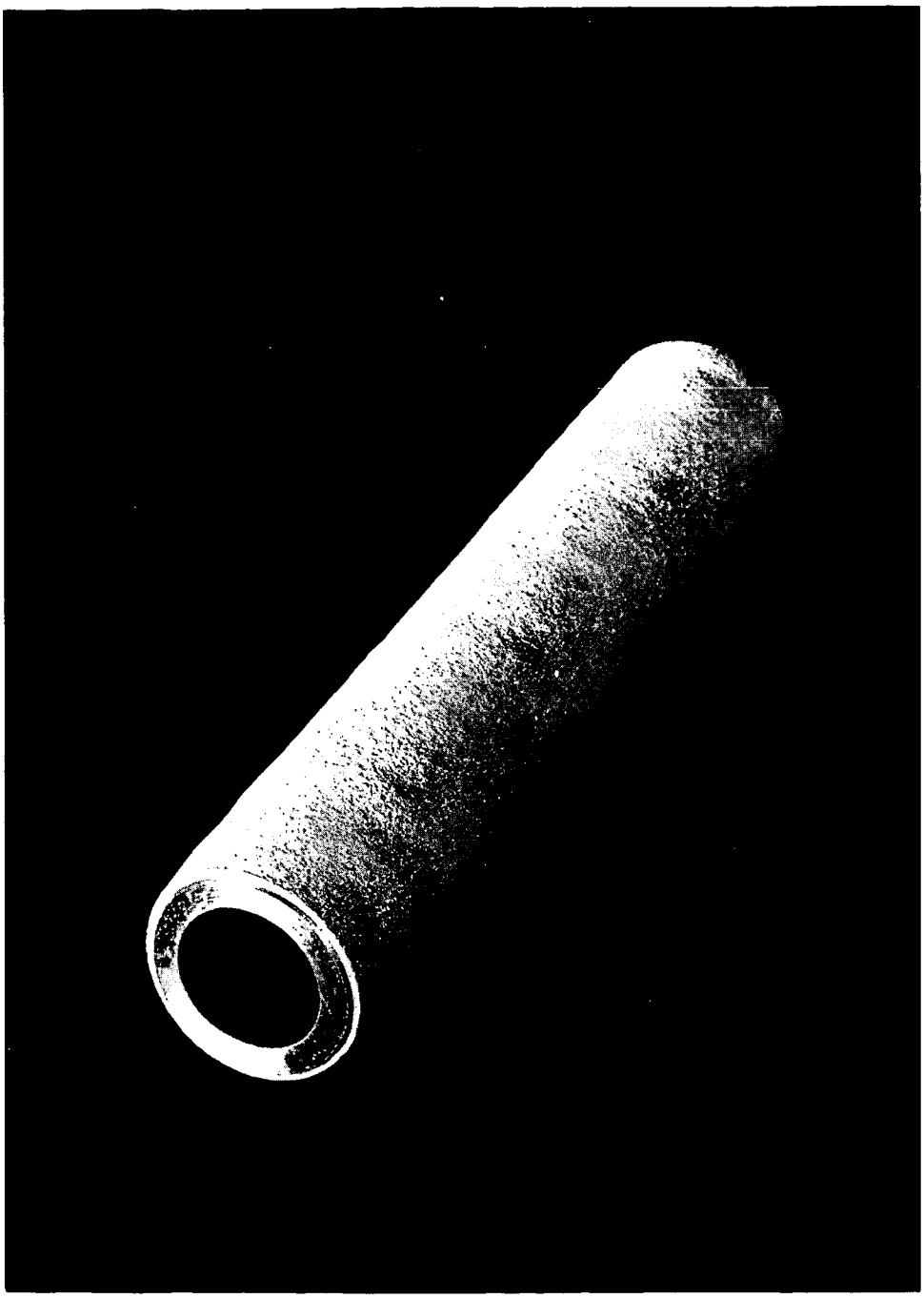


TABLE 5. - Results of bench-scale F.T. test compared to HGR-34

Experiment Number	HGR-34		FT-TW-1		
Fresh gas $\frac{\text{vol. gas, ft}^3/\text{hr}}{\text{Ft}^2 \text{ catalyst surface}}$	8.85	17.7	30	30	30
H_2/CO ratio in feed gas	1.4/1	1.4/1	3/1	3/1	3/1
Reactor pressure, psig	400	400	300	650	1,000
Catalyst temp. average °F/°C	608/320	617/325	615.2/324	602.6/317	609.9/318
H_2 Conversion, percent	90.1	83	40.32	43.67	45.12
CO Conversion, percent	98.2	94.4	78.30	78.46	76.21
H_2 + CO Conversion, percent	93.4	87.5	49.38	52.02	52.70
Heating value tail gas Btu/ft^3					
With CO_2	930	785	383	408	418
Without CO_2	1,000	852	419	447	453
Overall weight balance, percent	87.8	96.6	93.96	97.05	95.72
Hydrocarbons recovered lb/1000 scf fresh gas[1/]	10.3	11.6	4.148	5.139	5.714
Theoretical hydrocarbons, g/m^3(H_2 + CO) conversion	190.28	197.0	188.65	184.13	166.98
Recovery, percent	119.53	97.39	71.33	82.76	108.09
Hydrocarbon recovered, wt-pct					
$C_1 + C_2$	38.00	32.71	71.26	67.01	69.56
C_3	13.58	12.07	17.70	19.92	11.75
Gasoline ($C_3^{=}$ + <204°C)[1/]	48.11	50.01	9.18	12.14	18.32
Diesel Fuel (204° C- 316°C)	4.46	4.27	1.60	.83	.32
Fuel Oil (316°C-450°C)	.18	.52	.25	.10	.06
Wax (>450° C)	.11	.42	0.0	0.00	0.00

			Period					
Aqueous layer, grams/m^3(H_2 + CO)	Conv.		1st	2nd	1st	2nd	1st	2nd
C_1-C_4OH	4.34	6.11	3.16	4.34	7.70	17.14	30.34	42.33
Other oxygenates	.32	.36	.19	.13	.13	.18	0.0	0.0
H_2O	97.54	108.32	126.7	124.9	140.6	135.2	125.6	113.7
Percent CO in tail gas	4.21	9.67	8.09		8.0		8.3	

1/Includes alcohols and oxygenates.

CONCLUSION

We believe more work in the area of the Fischer-Tropsch reaction is needed. The process is very flexible; most any desired product can be obtained by selected reactor type, catalyst, operating temperature and synthesis gas ratio. Operating conditions can be easily changed to maximize the yield of product most in demand at any given time. Our work will continue to stress primarily the gasoline yield but oxygenates could be a desired byproduct.

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